

# Electron Electric Dipole Moment and Hyperfine Interaction Constants for ThO

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A recently implemented relativistic four-component configuration interaction approach to study  $\mathcal{P}$ - and  $\mathcal{T}$ -odd interaction constants in atoms and molecules is employed to determine the electron electric dipole moment effective electric field in the  $\Omega = 1$  first excited state of the ThO molecule. We obtain a value of  $E_{\text{eff}} = 75.6 \left[ \frac{\text{GV}}{\text{cm}} \right]$  with an estimated error bar of 3% and 10% smaller than a previously reported result [arXiv:1308.0414 [physics.atom-ph]]. Using the same wavefunction model we obtain an excitation energy of  $T_v^{\Omega=1} = 5329 \text{ [cm}^{-1}\text{]}$ , in accord with the experimental value within 2%. In addition, we report the implementation of the magnetic hyperfine interaction constant  $A_{||}$  as an expectation value, resulting in  $A_{||} = -1335 \text{ [MHz]}$  for the  $\Omega = 1$  state in ThO. The smaller effective electric field increases the previously measured upper bound to the electron electric dipole moment interaction constant [arXiv:1310.7534v2 [physics.atom-ph]] and thus mildly mitigates constraints to possible extensions of the Standard Model of particle physics.

## INTRODUCTION

Polar diatomic molecules are promising complex systems [1, 2] in search of the electric dipole moment (EDM) of the electron. The measurement of a non-zero permanent molecular EDM and the establishment of its origin in fundamental charge ( $\mathcal{C}$ ) and spatial parity ( $\mathcal{P}$ ) violating interactions [3], for example inducing an electron EDM, would be a signature of New Physics beyond the Standard Model (SM) of elementary particles [4].

The thorium monoxide (ThO) molecule has been found to be one of the most interesting candidates in this quest [5, 6], among other aspects due to its very large internal effective electric field  $E_{\text{eff}}$  on unpaired electrons [7]. Recently, the ACME collaboration reported an order of magnitude smaller upper bound to the electron EDM interaction constant,  $|d_e| < 8.7 \times 10^{-29} e \text{ cm}$ , obtained from a spin-precession measurement on a pulse of ThO molecules [8]. This upper bound for  $d_e$  is principally determined from Eq. (1),

$$d_e = \frac{\Delta E_t}{E_{\text{eff}}} \quad (1)$$

where  $\Delta E_t$  is an upper bound to a measured

transition energy and  $E_{\text{eff}}$  is the internal electric field at the position of the electron, giving rise to a dipolar interaction with the electron's postulated EDM.  $E_{\text{eff}}$  cannot be measured experimentally but has to be determined from a theoretical electronic-structure calculation on the respective molecule in the respective quantum state. On the one hand, large  $E_{\text{eff}}$  is a selection criterion for systems with a large EDM interaction and therefore holding promise for the electron EDM to actually be found. Second, an accurate value of  $E_{\text{eff}}$  is required for reliably constraining the parameter ranges of New Physics models going beyond the SM [9]. Great care is taken in assessing and minimizing errors in the determination of  $\Delta E_t$ . It is obvious that the same care should be taken in the theoretical assessment of the effective electric field  $E_{\text{eff}}$ .

Previous calculations of  $E_{\text{eff}}$  in the relevant "science" state  $\Omega = 1$ , arising mainly from the configuration  $7s^1 6d^1$  ( $\text{Th}^{2+} \text{O}^{2-}$ ), have been reported by Meyer et al. [7] and Skripnikov et al. [10]. In the former [7]  $E_{\text{eff}} = 104 \left[ \frac{\text{GV}}{\text{cm}} \right]$  has been obtained based on a semi-empirical model calculation which in part employs non-relativistic approximations and a very limited set of electronic configurations. The latter study [10] de-

termines  $E_{\text{eff}} = 84 \left[ \frac{\text{GV}}{\text{cm}} \right]$  by means of a two-component relativistic single-reference coupled cluster (CC) approach.

The work presented in this paper is aimed at an accurate determination of  $E_{\text{eff}}$  in the  $\Omega = 1$  excited state of the ThO molecule, along with a clarification of which physical aspects play the decisive role in obtaining this quantity reliably. In addition, we investigate the excitation energy of the  $\Omega = 1$  state and the parallel hyperfine coupling constant which is regarded as a measure of the quality of molecular wavefunctions employed in the determination of relativistic EDM enhancement factors.

## THEORY

### Electron EDM Hamiltonian

The potential energy due to the electron EDM interaction in the molecule is determined as an expectation value [11] over the one-body Hamiltonian  $\hat{H}_{\text{edm}}$  as follows

$$\begin{aligned} \left\langle \sum_{j=1}^N \hat{H}_{\text{edm}}(j) \right\rangle_{\psi} &= -d_e \left\langle \gamma^0 \sum_{j=1}^N \boldsymbol{\Sigma}_j \cdot \mathbf{E}_j \right\rangle_{\psi} \\ &= \frac{2icd_e}{e\hbar} \left\langle \gamma^0 \gamma^5 \sum_{j=1}^N \vec{p}_j^2 \right\rangle_{\psi} \end{aligned} \quad (2)$$

where  $N$  is the number of electrons,  $\gamma$  are the standard Dirac matrices,  $d_e$  is the electron EDM interaction constant,  $\boldsymbol{\Sigma} = \begin{pmatrix} \vec{\sigma} & \mathbf{0} \\ \mathbf{0} & \vec{\sigma} \end{pmatrix}$  with  $\vec{\sigma}$  the vector of Pauli spin matrices, and  $\mathbf{E}_j$  is the electric field at the position of an electron ( $j$ ). The wavefunction  $\psi$  is determined from relativistic 4-component Configuration Interaction (CI) theory [12] for the  $\psi_{\Omega=1}$  first electronically excited state of the ThO molecule, using the all-electron Dirac-Coulomb Hamiltonian. Details on the implementation of Eq. (2) can be found in reference 13. The optimized coefficients in the linear expansion of  $\psi$  in the basis of Slater determinants over 4-component Dirac spinors contain the approximate effects of electron correlations among the electrons explicitly treated in the CI expansion.

### Magnetic Hyperfine Interaction Constant

Since the magnetic vector potential  $\vec{A}$  due to the magnetic moment  $\vec{\mu}_K$  of a nucleus  $K$  at the

position  $\vec{r}$  of an electron in an atom is [14]

$$\vec{A} = \frac{\vec{\mu}_K \times \vec{r}}{r^3} \quad (3)$$

we can derive the parallel magnetic hyperfine interaction constant  $A_{||}$  as the  $z$  projection of the expectation value of the corresponding perturbative Hamiltonian in Dirac theory

$$A_{||} = \frac{\mu_{Th}}{I\Omega} \left\langle \sum_{i=1}^n \left( \frac{\vec{\alpha}_i \times \vec{r}_i}{r_i^3} \right)_z \right\rangle_{\psi} \quad (4)$$

where  $I$  is the nuclear spin quantum number,  $\alpha_k$  is a Hamiltonian-form Dirac matrix for particle  $k$ , and  $n$  is the number of electrons. Again, we evaluate Eq. (4) over the CI wavefunction for the state  $\psi_{\Omega=1}$ .

## APPLICATION TO THO

### Technical Details

#### General Setup

For the determination of the nuclear hyperfine coupling constant we use the thorium isotope  $^{229}\text{Th}$  for which the nuclear magnetic moment has been determined to be  $\mu = 0.45\mu_N$  [15]. Its nuclear spin quantum number is  $I = 5/2$ . In all calculations the speed of light was set to 137.0359998 a.u.

#### Atomic basis sets

Fully uncontracted atomic Gaussian basis sets of double- $\zeta$ , triple- $\zeta$  and quadruple- $\zeta$  quality were used for the description of electronic shells. For thorium we used Dyall's basis sets [16, 17] and for oxygen the Dunning cc-pVNZ-DK sets [18] with  $N \in \{2, 3, 4\}$ , as well as the aug-cc-pVTZ-DK set [18]. For thorium all  $5d, 5f, 7s, 6d$  correlating exponents were added to the basic  $n$ -tuple- $\zeta$  sets, amounting to  $\{26s, 23p, 17d, 13f, 1g\}$  uncontracted functions in case of double- $\zeta$  (in the following abbreviated as vDZ),  $\{33s, 29p, 20d, 14f, 4g, 1h\}$  in the case of triple- $\zeta$  (vTZ) and  $\{37s, 34p, 26d, 17f, 8g, 4h, 1i\}$  in the case of quadruple- $\zeta$  (vQZ), respectively. The latter set in addition contains all  $6s, 6p$  correlating exponents.

Molecular calculations were carried out with a modified local version of the `Dirac11` program package [19]. Optimized molecular spinors have been obtained using the Dirac-Coulomb Hamiltonian and all-electron four-component Hartree-Fock calculations. The basic model used for these open-shell calculations is based on an average-of-configuration Fock operator for two electrons in the Th ( $7s, 6d\delta$ ) Kramers pairs with all other (88) electrons restricted to closed shells. This model, called (av.2in3), denoting an averaging with 2 electrons in 3 Kramers pairs in the following, is appropriate for the region close to the equilibrium bond distance of the molecule where the dominant configurations correspond to the system  $\text{Th}^{2+}\text{O}^{2-}$  [20]. The open-shell averaging ensures a balanced description of the low-lying electronic states of interest in this study. In a few models using the smallest basis set (double- $\zeta$ ) the  $6d\pi\sigma$  and  $7p$  shells of Th were included due to partial mixing with the Th  $6d$  shell, defining (av.2in9). For the larger basis sets we have restricted the open-shell averaging to (av.2in3).

We exploit a Generalized Active Space (GAS) concept for defining CI wavefunctions of varying quality. Figure 1 shows the partitioning of the space of Kramers-paired spinors into seven subspaces, five of which are active for excitations. Based on this

partitioning and four parameters ( $m, n, p, q$ ) which define the accumulated occupation constraints of the subspaces, we choose four different CI wavefunction models for our calculations:

parameter values	correlation model label
$m = 2, n = 2, p = 0, q = 0$	$\text{MR}_K\text{-CISD}(18)$
$m = 3, n = 2, p = 0, q = 0$	$\text{MR}_K\text{-CISDT}(18)$
$m = 2, n = 2, p = 2, q = 0$	$\text{MR}_K\text{-CISD}(28)$
$m = 2, n = 2, p = 2, q = 2$	$\text{MR}_K\text{-CISD}(36)$

The parameter  $K$  (see Fig. 1) has been introduced to define variable active valence spinor spaces.  $K = 3$  includes only the Th ( $7s, 6d\delta$ ) spinors in the fourth active space and thus comprises a minimal model for a balanced description of the ground  $\Omega = 0$  state and the excited  $\Omega \in \{1, 2, 3\}$  states which derive from  $^3\Delta$  in the  $\Lambda$ - $S$  coupling picture. We have furthermore used  $K = 5$  which adds two  $\pi$ -type spinors to the fourth space,  $K = 7$  adding another two  $\pi$ -type spinors, and finally  $K = 9$

FIG. 1: Generalized Active Space models for ThO CI wavefunctions. The parameters  $m, n, p$  and  $q$  are defined in the text and determine the occupation constraints of the subspaces of Kramers-paired spinors. The molecular spinors are denoted according to their principal atomic character. The space with  $183 - K$  virtual Kramers pairs (for vTZ basis sets) is comprised by all canonical DCHF orbitals below an energy of  $38 E_H$ .

	# of Kramers pairs	accumulated # of electrons min. max.	
<b>Deleted</b>	<b>(176)</b>		
<b>Virtual</b>	<b>183-K</b>	<b>36</b>	<b>36</b>
<b>Th: <math>6d\sigma\pi, 7p, 8s</math> Th: <math>7s, 6d\delta</math></b>	<b>K</b>	<b>36-m</b>	<b>36</b>
<b>Th: <math>6s, 6p</math> O: <math>2s, 2p</math></b>	<b>8</b>	<b>34-n</b>	<b>34</b>
<b>Th: <math>5d</math></b>	<b>5</b>	<b>18-p</b>	<b>18</b>
<b>Th: <math>5s, 5p</math></b>	<b>4</b>	<b>8-q</b>	<b>8</b>
<b>Frozen core</b>	<b>(31)</b>		

and  $K = 10$  which adds energetically low-lying  $\sigma$ -type spinors to this space.

The different wavefunction models are in addition defined by the number of correlated electrons in total (in parenthesis) and the included excitation ranks, where “SDT” stands for Single, Double, and Triple excitations, as an example. The value of a parameter, e.g.  $p = 2$ , denotes the maximum hole rank of the respective active space. In that particular example all Slater determinants with zero up to two holes in the Th ( $5d$ ) space would be included in the wavefunction expansion.

### Electronic-structure results

We first establish molecular wavefunctions which accurately describe the excitation energy of the  $\Omega = 1$  electronic state. Table I displays vertical excitation energies as a function of basis set. The vTZ set leads to a large correction of  $-15\%$ , whereas the vQZ set only yields another  $-4\%$ , less than  $200 \text{ cm}^{-1}$  on the absolute. We therefore continue our investigation

with the set of vTZ quality.

The next criterion we consider is the electronic shells included in the explicit treatment of dynamic electron correlation. In Table II we compile results from only 2 correlated electrons (Th (7s, 6d) shells) up to 38 correlated electrons (Th (5s, 5p, 5d, 6s, 6p, 6d, 7s), O (2s, 2p) shells). Whereas correlations among the valence electrons of both atoms are seen to be important, core-valence and core-core correlations change the excitation energy by only  $-3\%$ , on the order of  $-100 \text{ cm}^{-1}$ .

As a third criterion we take the size and structure of the active spinor space into account.  $X$  giving the number of Kramers pairs in the active space, the excitation energies for four different models are compared in Table III. We observe that increasing the active space leads to non-negligible corrections. In particular the last step, from  $X = 7$  to  $X = 10$ , where  $\sigma$ -type spinors are added to the active space, proves to be important. It is only at this level that the vertical excitation energy becomes satisfactorily accurate as compared to the experimental value of  $T_e = 5317 \text{ cm}^{-1}$ . Theoretical studies have shown [20] that the difference between the equilibrium bond lengths in the  $\Omega = 0$  and the here considered  $\Omega = 1$  excited state amounts to only 0.03 a.u. From this result we infer a small non-parallelity correction on the order of  $-100 \text{ cm}^{-1}$  for our vertical excitation energy determined at the experimental minimum of the ground state potential-energy curve.

### Electron EDM and Hyperfine Interaction Constants

Having studied the quality of the wavefunction in describing the excited state of relevance to the electron EDM measurement, we turn our attention to the determination of the effective electric field and the hyperfine interaction constants in this state.

The results in Table I show that  $E_{\text{eff}}$  is virtually insensitive

to the size of employed atomic basis sets for ThO. The hyperfine interaction constant  $A_{||}$ , changes by hardly more than 1% in magnitude when increasing the basis set cardinal number from 2 to 4. Since increasing the cardinal number improves these standard basis sets predominantly in the outer core and valence atomic regions, we have also tested the effect of adding steep functions to the thorium atomic core. It is observed that  $E_{\text{eff}}$  changes no more than by 0.03%, depending on the respective Gaussian

TABLE I: Vertical excitation energy, effective electric field, and hyperfine constant at an internuclear distance of  $R = 3.477 \text{ a}_0$  for  $\Omega = 1$  using basis sets with increasing cardinal number and the wavefunction model MR<sub>3</sub>-CISD(18)

Basis set/CI Model	$T_v [\text{cm}^{-1}]$	$E_{\text{eff}} [\frac{\text{GV}}{\text{cm}}]$	$A_{  } [\text{MHz}]$
vDZ/MR <sub>3</sub> -CISD(18)	4535	80.8	-1283
vTZ/MR <sub>3</sub> -CISD(18)	3832	81.0	-1292
vQZ/MR <sub>3</sub> -CISD(18)	3643	80.7	-1298
Exp. ( $T_e$ ) <sup>a</sup>	5317		

<sup>a</sup>Reference [20]

exponent of the added function. In the work of Skripnikov et al. [10] diffuse functions are used in the atomic basis set for the oxygen atom, since the dominant contribution to the electronic states in question arise from  $\text{Th}^{2+} \text{O}^{2-}$  configurations [20], and therefore such diffuse functions may affect the present results. Replacing the oxygen vTZ basis set by the aug-cc-pVTZ-DK set leads to a change of  $E_{\text{eff}}$  of less than 0.01% and reduces  $T_v$  for  $\Omega = 1$  by only 32  $\text{cm}^{-1}$ . We therefore conclude that the vTZ basis set on the oxygen atom without additional diffuse functions yield sufficiently accurate results.

It has been argued that the EDM effective electric field is predominantly a core property [21] and thus could be sensitive to the correlated movement of the inner-shell electrons of the respective heavy atom. Table II suggests that these correlation contributions

TABLE II: Vertical excitation energy, effective electric field, and hyperfine constant at an internuclear distance of  $R = 3.477 \text{ a}_0$  for  $\Omega = 1$  correlating only the atomic valence shells down to including core-valence and core-core correlation and using the vTZ basis sets

CI Model	$T_v [\text{cm}^{-1}]$	$E_{\text{eff}} [\frac{\text{GV}}{\text{cm}}]$	$A_{  } [\text{MHz}]$
MR-CISD(2)	5929	68.5	-1264
MR <sub>3</sub> -CISD(18)	3832	81.0	-1292
MR <sub>3</sub> -CISD(28)	3752	80.0	-1297
MR <sub>3</sub> -CISD(36) <sup>a</sup>	3742	80.8	-1287
Exp. ( $T_e$ ) <sup>b</sup>	5317		

<sup>a</sup>Due to extreme computational demand the virtual cutoff is 5 a.u. here.

<sup>b</sup>Reference [20]

are negligible, at least for the ThO molecule. Whereas the inclusion of only the two valence electrons is insufficient for any of the properties

discussed here,  $E_{\text{eff}}$  and the hyperfine coupling constant prove to be sufficiently converged already at the valence level of 18 correlated electrons. As we have previously discussed for the  $\text{HfF}^+$  molecular ion [13] this can be rationalized as follows:

In orbital perturbation theory, the first-order corrected expression for a given spinor  $\varphi_i$  is

$$\varphi_i \approx \varphi_i^{(0)} + \sum_{k(\neq i)} \frac{\langle \varphi_k^{(0)} | \hat{V} | \varphi_i^{(0)} \rangle}{\varepsilon_i^{(0)} - \varepsilon_k^{(0)}} \varphi_k^{(0)} \quad (5)$$

where  $\varphi_m^{(0)}$  is the  $m$ th unperturbed spinor,  $\varepsilon_m^{(0)}$  the corresponding spinor energy and  $\hat{V}$  is the electron correlation fluctuation potential. In the present case we are interested in the change of the valence spinor  $\varphi_{7s}$  which is the dominant contributor to the electron EDM expectation value, Eq. (2). If a spinor  $\varphi_k^{(0)}$  is a(n) (outer) core spinor, the energy difference in the denominator will become very large and thus the correlation contribution to the form of the valence spinor will be very small. As an example, we consider  $\varphi_k^{(0)} = \varphi_{1s}$  and  $\varphi_i^{(0)} = \varphi_{7s}$ . The fluctuation potential matrix element  $\langle \varphi_k^{(0)} | \hat{V} | \varphi_i^{(0)} \rangle$  is on the order of  $E_H$ , whereas the energy denominator becomes  $\varepsilon_i^{(0)} - \varepsilon_k^{(0)} \approx (-0.05 + 4058.5) E_H = 4058.45 E_H$ . The perturbation coefficient of the  $\varphi_{1s}$  spinor to the  $\varphi_{7s}$  spinor is therefore strongly suppressed. This analysis is clearly confirmed by our results in Table II. Both  $E_{\text{eff}}$  and  $A_{||}$  are largely unaffected by including more than the 18 valence electrons in the explicit treatment of electron correlation. Even without having taken into account the innermost electronic shells of the thorium atom in the correlation treatment, we can conclude that such correlations, due to the increasing magnitude of the energy denominator in Eq. (5), will lead to negligible contributions to the wavefunction of valence spinors.

We now turn our attention to wavefunction models built from active spinor spaces of variable size, the results for which are given in Table III. The minimal active space (MR<sub>3</sub>-CISD) yields a value of  $E_{\text{eff}} = 81.0 \left[ \frac{\text{GV}}{\text{cm}} \right]$  which is quite close to the most elaborate result of Skripnikov et al. [10] which is  $84.0 \left[ \frac{\text{GV}}{\text{cm}} \right]$ . As expected, the augmentation of the active spinor space with spinors of different symmetry representation than  $\varphi_{7s}$  does not significantly affect  $E_{\text{eff}}$  for  $\Omega = 1$ . However, upon including the  $\sigma$ -type spinors in the active space, yielding the model MR<sub>10</sub>-CISD(18), we observe a strong drop of the effective electric field to a value of

TABLE III: Vertical excitation energy, effective electric field, and hyperfine constant at an internuclear distance of  $R = 3.477 a_0$  for  $\Omega = 1$  using the vTZ basis set and varying active spinor spaces

CI Model	$T_v$ [ $\text{cm}^{-1}$ ]	$E_{\text{eff}}$ [ $\frac{\text{GV}}{\text{cm}}$ ]	$A_{  }$ [MHz]
MR <sub>3</sub> -CISD(18)	3832	81.0	-1292
MR <sub>5</sub> -CISD(18)	4054	79.7	-1291
MR <sub>7</sub> -CISD(18)	4321	80.1	-1318
MR <sub>10</sub> -CISD(18)	5329	75.6	-1335
Exp. ( $T_e$ ) <sup>a</sup>	5317		

<sup>a</sup>Reference [20]

$75.6 \left[ \frac{\text{GV}}{\text{cm}} \right]$ . This reduction is accompanied by a striking improvement of the vertical excitation energy of the  $\Omega = 1$  state to a value in excellent agreement with the experimental result, even after applying the non-parallelity correction discussed earlier. The hyperfine constant exhibits an increase of slightly more than 3% in magnitude when increasing the size of the active spinor space from MR<sub>3</sub> to MR<sub>10</sub> which is a significantly larger change than those observed for different basis sets and varying number of correlated electrons.

In view of the significant discrepancy of the present MR<sub>10</sub>-CISD(18) result for  $E_{\text{eff}}$  from the value reported by Skripnikov et al. it is instructive to discuss the different wavefunction models that have led to these results. The fact that an increase of the size of the active space has a noticeable effect on a property of the molecule, here  $E_{\text{eff}}$  and  $A_{||}$ , points to the importance of a certain class of higher excitations in the molecular wavefunction expansion, here suggesting a multi-reference character of the  $\Omega = 1$  excited state. In order to gain more insight we have carried out additional studies including excitation ranks higher than Doubles into the virtual spinor space, see Table IV, which

TABLE IV: Vertical excitation energy, effective electric field, and hyperfine constant at an internuclear distance of  $R = 3.477 a_0$  for  $\Omega = 1$  using the vDZ basis set and varying maximum excitation rank

CI Model	$T_v$ [ $\text{cm}^{-1}$ ]	$E_{\text{eff}}$ [ $\frac{\text{GV}}{\text{cm}}$ ]	$A_{  }$ [MHz]
MR <sub>3</sub> -CISD(18)	4535	80.8	-1283
MR <sub>9</sub> -CISD(18)	5703	73.8	-1321
MR <sub>3</sub> -CISDT(18)	5166	74.4	-1340
Exp. ( $T_e$ ) <sup>a</sup>	5317		

<sup>a</sup>Reference [20]



was computationally feasible for the smallest employed basis sets, vDZ. Again, the inclusion of higher excitations leads to the characteristic drop in  $E_{\text{eff}}$ , here by  $\approx -6.5 \left[ \frac{\text{GV}}{\text{cm}} \right]$  (MR<sub>3</sub>-CISDT(18) relative to MR<sub>3</sub>-CISD(18)). Interestingly, nearly the same decrease is observed when configurations including three particles in the virtual space,  $v^3$ , are excluded from the CI expansion, model MR<sub>9</sub>-CISD(18), and the higher excitations are restricted to a subset involving additional  $\sigma$ -type spinors, i.e., configurations of the type  $\sigma^1 v^2$ . We note that the  $\Omega = 1$  excitation energy behaves in very similar way, with higher excitations involving the enlarged active spinor space playing the major role and increasing the excitation energy markedly (the overshooting value for MR<sub>9</sub>-CISD(18) is due to basis set incompleteness, as the results in Table I confirm). Also for  $A_{||}$  we observe a notable dependence on higher excitations in the wavefunction, to a large degree covered by the augmentation of the active spinor space. Again, the most elaborate result of Skripnikov et al. ( $-1296 \text{ [MHz]}$  in our units) is very close to our result using the insufficient active spinor space ( $-1292 \text{ [MHz]}$ ).

Apparently, it is configurations involving excitations into the augmenting active space spinors, combined with correlation excitations into the virtual space that are of major importance for obtaining an accurate value for  $E_{\text{eff}}$ , and not the higher excitations such as  $v^3$  provided by the Coupled Cluster (CC) model of Skripnikov et al. The CC model of the latter authors, in turn, is a standard single-reference CC expansion which is applied to the property of an electronically excited state which clearly exhibits a significant multi-reference character, as our results demonstrate. In addition, Skripnikov et al. use ground-state  $^1\Sigma_0$  spinors and the same state as the Fermi vacuum for the CC expansion which biases the wavefunction towards this ground state. This is confirmed by the too high excitation energy of the  $\Omega = 1$  state obtained by those authors ( $5741 \text{ cm}^{-1}$ ) as compared to the experimental value of  $5317 \text{ cm}^{-1}$ . In contrast to this result, our best model vTZ/MR<sub>10</sub>-CISD(18) which is in addition based on configuration-averaged spinors yields an excitation energy in much better agreement with the experimental value, and, furthermore, shows that the adequate description of all relevant physical effects results in a value of  $E_{\text{eff}} = 75.6 \left[ \frac{\text{GV}}{\text{cm}} \right]$ , 10% smaller than the earlier prediction of Skripnikov et al.

## CONCLUSION

By means of a careful study of effects due to basis sets, dynamic electron correlation, and active spinor spaces within a rigorously relativistic all-electron four-component formalism, we have determined the EDM effective electric field for the  $\Omega = 1$  first electronically excited state at the experimental internuclear distance for the ThO molecular ground state. We obtain a value of  $E_{\text{eff}} = 75.6 \left[ \frac{\text{GV}}{\text{cm}} \right]$  with an estimated error bar of 3% and 10% smaller than the result previously reported by others [10]. With the same wavefunction model we have obtained an excitation energy for the  $\Omega = 1$  state of  $T_v = 5329 \text{ cm}^{-1}$ , in excellent agreement with the experimental result which confirms the quality of the molecular wavefunctions employed in the present study of  $\mathcal{P}$  and  $\mathcal{T}$  violating effects in ThO. The magnetic hyperfine interaction constant is obtained to  $A_{||} = -1335 \text{ [MHz]}$  using our most reliable wavefunction model. Our detailed analysis shows that the ThO  $\Omega = 1$  state has a strong multi-reference nature which must be adequately accounted for in electronic-structure theoretical treatments.

Our result for  $E_{\text{eff}}$  has consequences for the recently determined upper bound to the electron EDM interaction constant of  $|d_e| < 8.7 \times 10^{-29} e \text{ cm}$  [8]. This upper bound has been obtained based on  $E_{\text{eff}} = 84 \left[ \frac{\text{GV}}{\text{cm}} \right]$  [10]. Due to Eq. (1) a 10% smaller value for  $E_{\text{eff}}$  requires a corresponding adjustment of the upper bound for  $d_e$  to a larger value. Consequently, the electron EDM constraint to models extending the Standard Model of elementary particles is somewhat attenuated.

In ongoing work we are studying potential energy curves for ThO along with dipole and transition dipole moments for relevant molecular electronic states. Furthermore, we are continuing with the implementation of further operators of importance in the search for  $\mathcal{P}$  and  $\mathcal{T}$  violating effects in the universe, in particular the scalar-pseudoscalar  $\mathcal{P}, \mathcal{T}$ -odd electron-nucleon interaction.

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